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| ETHYLENIC RANDOM COPOLYMER WAX AND | | 2-9, Muronoki-machi 1-chome, Iwakuni-shi, | |
| PROCESS FOR PRODUCTION THEREOF | | Yamaguchi, JAPAN | |
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SPECIFICATION

1. Title of the invention

5 ETHYLENIC RANDOM COPOLYMER WAX AND PROCESS FOR PRODUCTION
THEREOF

2. Claim

1. An ethylenic random copolymer wax consisting
10 essentially of units derived from ethylene and an alpha-olefin
having 3 to 20 carbon atoms, said copolymer wax being
characterized in that

(a) it has an ethylene unit content in the range of 85
to 99 mole% and an alpha-olefin unit content in the range of
15 1 to 15 mole%,

(b) it has an intrinsic viscosity $[\eta]$, measured in

decalin at 135°C, of 0.02 to 0.5dl/g,

(c) it has a molecular weight distribution (M_w/M_n), determined by gel permeation chromatography, of not more than 2.5,

5 (d) it has a crystallinity, determined by X-ray diffraction method, of 5 to 85%,

(e) it has a B value, defined by the following equation (I), within the range defined by the following equation (II)

$$B \equiv \frac{P_{OE}}{2 P_O \cdot P_E} \quad (I)$$

10 wherein P_E represents the molar fraction of the ethylene component in the copolymer, P_O is the molar fraction of the alpha-olefin component in the copolymer, P_{OE} is the molar fraction of alpha-olefin/ethylene chains in the total dyad chains,

$$15 \quad 1.00 \leq B \leq 2 \quad (II)$$

(f) signals of $\alpha\beta$ and $\beta\gamma$ based on a methylene chain between two adjacent tertiary carbon atoms in the main chain of the copolymer are not observed in the ^{13}C -NMR spectrum of the copolymer.

20

2. A process for producing an ethylenic random copolymer wax consisting essentially of units derived from ethylene and an alpha-olefin having 3 to 20 carbon atoms, comprising

copolymerizing ethylene and an alpha-olefin having 3 to 20 carbon atoms in the presence of a catalyst comprising

(A) a zirconium hydride compound containing a group having conjugated π electrons as a ligand and

5 (B) an aluminoxane,

said copolymer wax being characterized in that

(a) it has an ethylene unit content in the range of 85 to 99 mole% and an alpha-olefin unit content in the range of 1 to 15 mole%,

10 (b) it has an intrinsic viscosity $[\eta]$, measured in decalin at 135°C, of 0.02 to 0.5dl/g,

(c) it has a molecular weight distribution (M_w/M_n), determined by gel permeation chromatography, of not more than 2.5,

15 (d) it has a crystallinity, determined by X-ray diffraction method, of 5 to 85%,

(e) it has a B value, defined by the following equation (I), within the range defined by the following equation (II)

$$B \equiv \frac{P_{OE}}{2 P_O \cdot P_E} \quad (I)$$

20 wherein P_E represents the molar fraction of the ethylene component in the copolymer, P_O is the molar fraction of the alpha-olefin component in the copolymer, P_{OE} is the molar fraction of alpha-olefin/ethylene chains in the total dyad

chains,

$$1.00 \leq B \leq 2 \quad (\text{II})$$

(f) signals of $\alpha\beta$ and $\beta\gamma$ based on a methylene chain between two adjacent tertiary carbon atoms in the main chain of the copolymer are not observed in the ^{13}C -NMR spectrum of the copolymer.

3. DETAILED DESCRIPTION OF THE INVENTION

FIELD OF INDUSTRIAL APPLICATION

This invention relates to an ethylenic random copolymer wax and a process for its production. More specifically, it relates to an ethylenic random copolymer wax having a narrow molecular weight distribution, a narrow composition distribution, low surface stickiness, a low melting point and a low softening point, and a process for its production.

10 PRIOR ART

Ethylenic polymer waxes have been widely used for applications such as various dispersing agents, water-based dispersing agents, modifiers or toners for electrostatic copy. In some fields or applications, ethylenic polymer waxes having a low density, a low melting point and a low softening point have been desired. Ethylene/alpha-olefin random copolymer waxes are used in these fields. In any case of them, ethylenic polymer waxes having a narrow molecular weight distribution, a narrow composition distribution, low surface stickiness and low cohesiveness are desired. At present, in the fields of dispersing agents, water-based dispersing agents, modifiers and toners for electrostatic copy, an ethylene/alpha-olefin random copolymer waxes having especially a low density, a low melting point and a low softening point, and being superior

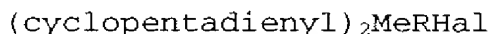
in the above properties, are strongly desired.

Till now, ethylenic polymer waxes have been widely known to be produced by methods comprising (co)polymerizing ethylene in the presence of a titanium-type catalyst composed of a titanium compound and an organoaluminum compound or a vanadium-type catalyst composed of a vanadium compound and an organoaluminum compound. Copolymer waxes produced by the method comprising (co)polymerizing ethylene with an alpha-olefin in the presence of a titanium-type catalyst generally have poor randomness, a broad molecular weight distribution and a broad composition distribution, and their properties of surface stickiness and cohesiveness are unsatisfactory. Ethylene/alpha-olefin random copolymer waxes obtained in the presence of the vanadium-type catalyst have higher randomness, a narrower molecular weight distribution and a narrower composition distribution than those obtained in the presence of the titanium-type catalyst. And ethylene/alpha-olefin random copolymer waxes obtained in the presence of the vanadium-type catalyst have a lower density, a lower melting point and a lower softening point than those obtained in the presence of the titanium-type catalyst having a same alpha-olefin unit content. These polymer waxes are, however, still unsatisfactory for the application which must meet rigorous requirements of the above properties and it is

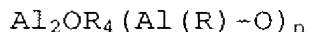
desired to improve the quality of such copolymer waxes.

On the other hand, a catalyst composed of a zirconium compound and an aluminoxane has been proposed as a novel Ziegler-type olefin polymerization catalyst in the next prior art documents. However, an ethylene/alpha-olefin random copolymer wax was not described in any of these prior art documents.

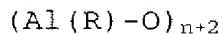
Japanese Laid-Open Patent Publication No.19309/1983 describes a process which comprises polymerizing ethylene and at least one alpha-olefin having 3 to 12 carbon atoms at a temperature of -50 to 200°C in the presence of a catalyst comprising a transition metal-containing compound represented by the following formula



wherein R is cyclopentadienyl, C₁-C₆ alkyl or halogen, Me is a transition metal, and Hal is halogen, and a linear aluminoxane represented by the following formula



wherein R is methyl or ethyl and n is a number of 4 to 20, or a cyclic aluminoxane represented by the following formula

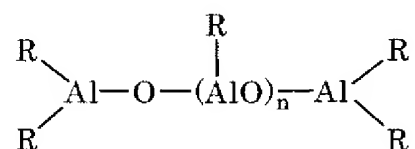


wherein R and n are as defined.

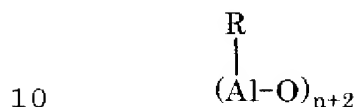
This patent document states that to control the density of the resulting polyethylene, ethylene should be polymerized in the

presence of a small amount (up to 10% by weight) of an alpha-olefin having a somewhat long chain or a mixture of such alpha-olefins.

Japanese Laid-Open Patent Publication No. 95292/1984
5 describes a process for producing a linear aluminoxane represented by the formula



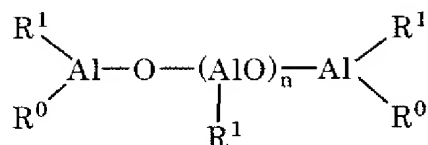
wherein n is 2 to 40 and R is a C₁-C₆ alkyl,
and cyclic aluminoxanes of the formula



wherein n and R are as defined.

The patent document states that if ethylene is polymerized in the presence of a mixture of methylaluminoxane produced by the process described in it with a bis(cyclopentadienyl) compound
15 of titanium or zirconium, polyethylene is obtained in an amount of at least 25 million grams/hour gram of transition metal.

Japanese Laid-Open Patent Publication No. 35005/1985 discloses a process for producing an olefin polymerization catalyst which comprises reacting an aluminoxane compound
20 represented by the following formula



wherein R^1 is C1-C10 alkyl, R^0 is R^1 or R^0 and R^1 together represent -O-,

with a magnesium compound, chlorinating the reaction product,

5 and further treating the chlorination product with a compound of Ti, V, Zr or Cr. The patent document states that the resulting catalyst is suitable for copolymerizing a mixture of ethylene and a C_3 - C_{12} alpha-olefin.

Japanese Laid-Open Patent Publication No. 35,006/1985

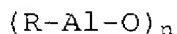
10 discloses a combination of (a) a mono-, di- or tri-cyclopentadienyl of two or more different transition metals or derivatives thereof and (b) alumoxane (aluminumoxane) as a catalyst for producing a blended polymer in a reactor. Example 1 of this patent document discloses that polyethylene

15 having a number average molecular weight of 15,300, a weight average molecular weight of 36,400 and a propylene content of 3.4% was obtained by polymerizing ethylene and propylene using bis(pentamethylcyclopentadienyl)zirconium dimethyl and alumoxane as a catalyst. Example 2 of this patent document

20 states that a blend of polyethylene and ethylene/propylene copolymer which has a number average molecular weight of 2,000, a weight average molecular weight of 8,300 and a propylene

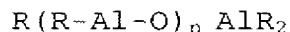
content of 7.1 mole% and consists of a toluene-soluble portion having a number average molecular weight of 2,200, a weight average molecular weight of 11,900 and a propylene content of 30 mole% and a toluene-insoluble portion having a number average molecular weight of 3,000, a weight average molecular weight of 7,400 and a propylene content of 4.8 mole% was obtained by polymerizing ethylene and propylene using bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride and alumoxane as catalyst. Likewise, Example 3 describes a blend of LLDPE and an ethylene/propylene copolymer which consists of a soluble portion having a molecular weight distribution (Mw /Mn) of 4.57 and a propylene content of 20.6 mole% and an insoluble portion having a molecular weight distribution of 3.04 and a propylene content of 2.9 mole%.

Japanese Laid-Open Patent Publication No. 35007/1985 discloses a process which comprises polymerizing ethylene alone or with an alpha-olefin having at least 3 carbon atoms in the presence of a catalyst comprising a metallocene and a cyclic alumoxane of the following formula



wherein R is an alkyl group having 1 to 5 carbon atoms, and n is an integer of 1 to 20,

or a linear alumoxane of the following formula



wherein R and n are as defined.

The polymer obtained by this process has a weight average molecular weight of about 500 to about 1,400,000 and a molecular weight distribution of 1.5 to 4.0 as described in this patent document.

Japanese Laid-Open Patent Publication No. 35008/1985 describes that by using a catalyst system comprising an alumoxane and at least two metallocenes, polyethylene or a copolymer of ethylene and a C₃-C₁₀ alpha-olefin having a broad molecular weight distribution is produced. This patent document states that the above copolymer has a molecular weight distribution of 2 to 50.

15 PROBLEMS TO BE SOLVED BY THE INVENTION

It is an object of this invention to provide a novel ethylenic random copolymer wax.

Another object of this invention is to provide an ethylenic random copolymer wax having a narrow molecular weight distribution, a narrow composition distribution, low surface stickiness, a low melting point and a low softening point.

Still another object of this invention is to provide an ethylenic random copolymer wax having a narrow molecular

weight distribution and only a small amount of low molecular weight component which makes the molecular weight distribution curve wide-based in shape, therefore having low stickiness and cohesiveness.

5 Yet another object of this invention is to provide an ethylenic random copolymer wax, which has an excellent ability to disperse powder such as pigment, therefore suitable for a dispersing agent (e.g. pigment dispersing agent) or a modifier.

10 Additional object of this invention is to provide a process for producing the aforesaid ethylenic random copolymer wax.

Other objects of this invention along with its advantages will become apparent from the following description.

15

MEANS FOR SOLVING PROBLEMS AND ITS EFFECTS

These objects and advantages of this invention are achieved in accordance with this invention by an ethylenic random copolymer wax consisting essentially of units derived
20 from ethylene and an alpha-olefin having 3 to 20 carbon atoms, said copolymer wax being characterized in that

(a) it has an ethylene unit content in the range of 85 to 99 mole% and an alpha-olefin unit content in the range of 1 to 15 mole%,

(b) it has an intrinsic viscosity $[\eta]$, measured in decalin at 135°C, of 0.02 to 0.5dl/g,

(c) it has a molecular weight distribution (M_w/M_n), determined by gel permeation chromatography, of not more than
5 2.5,

(d) it has a crystallinity, determined by X-ray diffraction method, of 5 to 85%,

(e) it has a B value, defined by the following equation (I), within the range defined by the following equation (II)

$$10 \quad B \equiv \frac{P_{OE}}{2 P_O \cdot P_E} \quad (I)$$

wherein P_E represents the molar fraction of the ethylene component in the copolymer, P_O is the molar fraction of the alpha-olefin component in the copolymer, P_{OE} is the molar fraction of alpha-olefin/ethylene chains in the total dyad
15 chains,

$$1.00 \leq B \leq 2 \quad (II)$$

(f) signals of $\alpha\beta$ and $\beta\gamma$ based on a methylene chain between two adjacent tertiary carbon atoms in the main chain of the copolymer are not observed in the ^{13}C -NMR spectrum of the
20 copolymer.

According to this invention, the ethylenic random copolymer wax of the invention can be produced by the process which comprises copolymerizing ethylene and an alpha-olefin

having 3 to 20 carbon atoms in the presence of a catalyst comprising (A) a zirconium hydride compound containing a group having conjugated π electrons as a ligand and (B) an aluminoxane.

5 The zirconium hydride compound (A) may, for example, be a compound represented by the following formula (III)



wherein R_1 represents an cycloalkadienyl group, R_2 and R_3 represent cycloalkadienyl groups, aryl groups, alkyl groups,
10 halogen atoms or hydrogen atoms.

Examples of the cycloalkadienyl group include cyclopentadienyl, methylcyclopentadienyl, ethylcyclopentadienyl, dimethylcyclopentadienyl, indenyl and tetrahydroindenyl groups.

15 Examples of the alkyl groups of R_2 and R_3 include methy, ethyl, propyl, isopropyl and butyl groups. Examples of the aryl group include phenyl, benzyl and neophyl groups. Examples of the halogen atom include fluorine, chlorine and bromine atoms. Examples of the zirconium hydride compound include

20 bis(cyclopentadienyl)zirconium monochloride monohydride,
bis(cyclopentadienyl)zirconium monobromide monohydride,
bis(cyclopentadienyl)methylzirconium hydride,
bis(cyclopentadienyl)ethylzirconium hydride,
bis(cyclopentadienyl)cyclohexylzirconium hydride,

bis(cyclopentadienyl)phenylzirconium hydride,
bis(cyclopentadienyl)benzylzirconium hydride,
bis(cyclopentadienyl)neobenzylzirconium hydride,
bis(methylcyclopentadienyl)zirconium monochloride

5 monohydride and

bis(indenyl)zirconium monochloride monohydride.

The zirconium hydride compounds may be used directly. Preferably, those zirconium hydride compounds which are difficultly soluble in solvents such as toluene (for example,
10 bis(cyclopentadienyl)zirconium monochloride monohydride) are used after they are contacted with organoaluminum compounds. This operation renders the sparingly solvent-soluble zirconium hydride compounds readily soluble in solvents.

Specific examples of the organoaluminum compound to be
15 contacted with the zirconium hydride compounds include trialkyl aluminums such as trimethyl aluminum, triethyl aluminum and tributyl aluminum; trialkenyl aluminums such as triisoprenyl aluminum; dialkyl aluminum alkoxides such as dimethyl aluminum methoxide, diethyl aluminum ethoxide and
20 dibutyl aluminum butoxide; alkyl aluminum sesquialkoxides such as methyl aluminum sesquimethoxide and ethyl aluminum sesquiethoxide; partially alkoxyated alkyl aluminums having the average composition of the formula $R^{1}_{2.5}Al(OR^2)_{0.5}$; partially halogenated alkyl aluminums, for example dialkyl aluminum

halides such as dimethyl aluminum chloride, diethyl aluminum chloride and dimethyl aluminum bromide, alkyl aluminum sesquihalides such as methyl aluminum sesquichloride and ethyl aluminum sesquichloride, and alkyl aluminum dihalides such as
 5 methyl aluminum dichloride and ethyl aluminum dichloride.

Preferably, the reaction of the two compounds is carried out in a hydrocarbon solvent while shutting off light. The mole ratio of the organoaluminum compound and the zirconium compound (Al/Zr) is from 0.5 to 30, preferably from 1 to 20.
 10 The concentration of zirconium is 0.001 to 1 mole, preferably about 0.005 to 0.1 mole, per liter of the liquid phase. The reaction temperature is about 0 to 120°C. The above hydrocarbon solvent can be selected from the after-mentioned examples of a solvent for polymerization.

15 Specific examples of the aluminoxane (B) as an ingredient constituting the catalyst used in this invention are organoaluminum compounds represented by the following general formula (IV) or (V)



wherein R represents a hydrocarbon group, and m represents an integer of 25 or more. In these aluminoxanes, R is a hydrocarbon

group such as methyl, ethyl, propyl or butyl group, preferably a methyl or ethyl group, especially preferably a methyl group. m is an integer of 25 or more, preferably 30 or more, especially preferably 35 to 100. The aluminoxanes may be prepared, for
5 example, by the following methods.

(1) A method which comprises adding a trialkyl aluminum in a suspension of a compound containing water of adsorption or a salt containing water of crystallization, for example, magnesium chloride hydrate, copper sulfate hydrate or aluminum
10 sulfate hydrate, in a hydrocarbon medium, and reacting the compounds.

(2) A method which comprises reacting a trialkyl aluminum directly with water in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

15 The method (1) is preferred. The aluminoxanes used in this invention may permissibly contain small amounts of organometallic components.

In the process of this invention, the starting material to be fed to the polymerization reaction system is a mixture
20 of ethylene and an alpha-olefin having 3 to 20 carbon atoms. The content of ethylene in the starting material is usually 50 to 97 mole%, preferably 60 to 95 mole%, and the content of the alpha-olefin is usually 3 to 50 mole%, preferably 5 to 40 mole%. Therefore the olefin as a starting material for

polymerization is a mixture of ethylene and an alpha-olefin.

Specific examples of the alpha-olefin having 3 to 20 carbon atoms used in the starting material in the process of this invention are propylene, 1-butene, 1-hexene, 5 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicocene.

The polymerization reaction of the olefins in the process of this invention is usually carried out in a hydrocarbon solvent. Specific examples of the hydrocarbon solvent are 10 aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and 15 petroleum fractions such as gasoline, kerosene and light oils. The starting olefins may themselves serve as the hydrocarbon medium. Among these hydrocarbon media, the aromatic hydrocarbons are preferably used in the process of this invention.

20 In the process of this invention, liquid phase polymerization methods such as a suspension polymerization method or solution polymerization method are usually adopted. Especially preferably a solution polymerization method is adopted. The polymerization temperature is 20 to 200°C,

preferably 30 to 150°C, especially preferably 40 to 120°C.

The proportion of the zirconium hydride compound (A) used in practicing the process of this invention in a liquid phase polymerization method is usually 10^{-8} to 10^{-2} gram-atom/liter, preferably 10^{-7} to 10^{-3} gram-atom/liter, as the concentration of the zirconium atom in the polymerization reaction system. The proportion of the aluminoxane (B) used is usually 10^{-4} to 10^{-1} gram-atom/liter, preferably 10^{-3} to 5×10^{-2} gram-atom/liter, as the concentration of the aluminum atom in the polymerization reaction system. The ratio of the aluminum atom to the zirconium atom in the polymerization reaction system is generally in the range of 25 to 10^7 , preferably 10^2 to 10^6 . The molecular weight of the copolymer can be controlled by using hydrogen, and/or by adjusting the polymerization temperature.

After the polymerization reaction by the process of this invention, the polymerization reaction mixture is worked up in a customary manner to give the ethylenic random copolymer wax of the invention.

The ethylenic random copolymer wax of this invention has an ethylene unit content in the range of 85 to 99 mole%, preferably 88 to 98 mole%, and an alpha-olefin unit content of 1 to 15 mole%, preferably 2 to 12 mole%.

The ethylenic random copolymer wax of this invention has an intrinsic viscosity $[\eta]$, measured in decalin at 135°C, of

usually 0.02 to 0.5dl/g, preferably 0.03 to 0.4dl/g.

The ethylenic random copolymer wax of this invention has a molecular weight distribution (M_w/M_n), measured by gel permeation chromatography (GPC), of not more than 2.5, preferably not more than 2.2, especially preferably not more than 2. If the molecular weight distribution of the ethylenic copolymer wax is greater than 2.5, the copolymer or the composition containing the copolymer as a modifier has more stickiness or causes blocking. Therefore it is necessary that the molecular weight distribution is in the range mentioned above.

The molecular weight distribution is measured as follows in accordance with Takeuchi, "Gel Permeation Chromatography" published by Maruzen Co., Ltd., Tokyo.

(1) The GPC count of standard polystyrene (monodisperse polystyrene made by Toyo Soda Co., Ltd.) of known molecular weight M is measured, and a calibration curve for the molecular weight M versus the elution volume is drawn. The concentration of standard polystyrene at this time is adjusted to 0.02% by weight.

(2) A gel permeation chromatograph of a sample polymer is taken by GPC measurement. From the calibration curve mentioned in (1) above, the number average molecular weight M_n and the weight average molecular weight M_w of the sample

are calculated. The M_w / M_n is thus obtained. The conditions for sample preparation and GPC measurement are as follows:

[Sample preparation]

(a) The sample is put in an Erlenmeyer flask together
5 with o-dichlorobenzene as a solvent so that its concentration becomes 0.1% by weight.

(b) An antioxidant (2,6-di-tert-butyl-p-cresol) is added in an amount of 0.05% by weight based on the polymer solution in the Erlenmeyer flask containing the sample.

10 (c) The Erlenmeyer flask is heated to 140°C, and the mixture is stirred for about 30 minutes to form a solution.

(d) The polymer solution is subjected to GPC.

[GPC measurement]

The measurement is conducted under the following
15 conditions.

(a) Device: 150C-ALC/GPC made by Waters Co.

(b) Column: ZORBAX PSM BiModal-s made by Du Pont Co.

(c) Amount of the sample: 200 microliters

(d) Temperature: 140°C

20 (e) Flow rate: 1 ml/min.

The ethylenic random copolymer wax has a crystallinity, determined by X-ray diffraction method, of 5 to 85%, preferably 10 to 80%, especially preferably 20 to 70%.

Furthermore, the ethylenic random copolymer wax of this

invention has a B value, defined by the following equation (I),
 within the range defined by the following equation (II)

$$B \equiv \frac{P_{OE}}{2 P_O \cdot P_E} \quad (I)$$

wherein P_E represents the molar fraction of the ethylene
 5 component in the copolymer, P_O is the molar fraction of the
 alpha-olefin component in the copolymer, P_{OE} is the molar
 fraction of alpha-olefin/ethylene chains in the total dyad
 chains [these molar fractions in equation (I) are calculated
 after excluding the terminal components],

$$10 \quad 1.00 \leq B \leq 2 \quad (II)$$

The B value is an index showing the state of distribution
 of the individual monomer components in the copolymer chain,
 and can be calculated from P_E , P_O and P_{OE} which are measured
 on the basis of G. J. Ray, *Macromolecules*, 10, 773 (1977), J.
 15 C. Randall, *Macromolecules*, 15, 353 (1982), J. Polymer Science,
 Polymer Physics Ed., 11, 275 (1973), and K. Kimura, *Polymer*,
 25, 441 (1984).

As the B value is larger, the copolymer has higher
 alternateness between ethylene and alpha-olefin and a more
 20 uniform distribution of ethylene and alpha-olefin and a
 narrower composition distribution.

Preferably, the ethylenic random copolymer wax of this
 invention has the following B values.

$$1.3-0.3 \times P_E \leq B \leq 1/P_E,$$

more preferably

$$1.4-0.4 \times P_E \leq B \leq 1/P_E,$$

especially preferably

5
$$1.5-0.5 \times P_E \leq B \leq 1/P_E.$$

The B value is determined as follows: A sample is prepared by uniformly dissolving about 200 mg of the copolymer in 1 ml of hexachlorobutadiene in a sample tube having a diameter of 10 mm. The ^{13}C -NMR spectrum of the sample is usually measured
10 under the following conditions.

Temperature: 120°C

Frequency: 25.0 MHz

Spectral width: 1500 Hz

Filter width: 1500 Hz

15 Pulse repeating time: 4.2 sec

Pulse width: 7 μsec

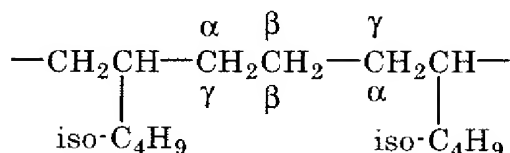
Integration cycles: 2000 to 5000

P_E , P_O and P_{OE} are determined from the spectrum, and the B value is calculated from them.

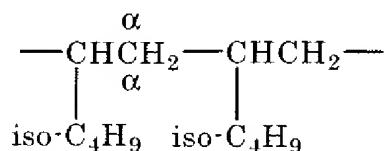
20 In the ^{13}C -NMR spectrum of the ethylenic random copolymer wax of this invention, signals of $\alpha\beta$ and $\beta\gamma$ based on a methylene chain between two adjacent tertiary carbon atoms in the main chain of the copolymer are substantially not observed.

For example, in the following bond of a copolymer of

ethylene and 4-methyl-1-pentane, the three central methylene groups are at the positions of α , β , and γ from left when viewed from the left tertiary carbon derived from 4-methyl-1-pentane, and on the other hand, at the positions of α , β , and γ from right when viewed from the right tertiary carbon. Hence, the
 5 above bond unit contains methylene groups which give signals of $\alpha\gamma$ and $\beta\beta$, but contains no methylene group which gives signals of $\alpha\beta$ and $\beta\gamma$.

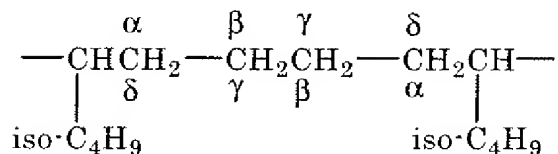


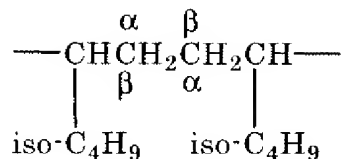
10 Likewise, in the following bond in which 4-methyl-1-pentane are bonded by head-to-tail



only methylene groups which give signals of $\alpha\alpha$ exist, and there is no methylene group which gives a signal of $\alpha\beta$ and $\beta\gamma$.

15 On the other hand, the following bonds





have methylene groups which give a signal of $\beta\gamma$ and a signal of $\alpha\beta$.

It is apparent from the foregoing description, in the
 5 ethylenic random copolymer wax of this invention, the direction of bonding of a monomer copolymerizable with ethylene is regular.

The ethylenic random copolymer wax of this invention usually has a density of not more than 0.95 g/cm^3 , preferably
 10 0.87 to 0.94 g/cm^3 . The density was measured in a density-gradient tube with the sample which had been melted at 150°C , and maintained at this temperature for 1 hour and then at room temperature for 3 hours.

The highest melting point of the ethylenic random
 15 copolymer wax of this invention measured by a differential scanning calorimeter is usually in the range of 60 to 120°C (cf. Figure 1). The relationship between the density (D) and the highest melting point (T_m) is

$$T_m \leq 300 \times D - 162 \text{ } (^\circ\text{C})$$

20 more preferably

$$T_m \leq 400 \times D - 256 \text{ } (^\circ\text{C}).$$

The measurement is carried out by the differential scanning

calorimeter (DSC-II made by PERKIN-ELMER Co.). About 5mg of the sample wax was charged into the sample case and weighed, then put in the calorimeter. The sample wax was maintained at 200°C for 5 minutes, then gradually cooled to 20°C at the rate of 20°C/min.

The absorption spectrum was obtained by gradually heating this sample wax at the rate of 10°C/min, an example of which was shown in Figure 1.

The softening point of the ethylenic random copolymer wax of this invention measured in accordance with JIS K 2531 R&B is usually 70 to 125°C, preferably 75 to 120°C.

The ethylenic random copolymer wax of this invention usually has an iodine value of 0.1 to 50.

The ethylenic random copolymer wax of this invention has a narrower molecular weight distribution, a narrower composition distribution, and smaller amount of low molecular weight component which makes the molecular weight distribution curve wide-based in shape than those of the copolymer obtained with a titanium-type catalyst.

The molecular weight distribution and the composition distribution of the copolymer wax of this invention are nearly equal or narrower than those of the copolymer obtained with a vanadium-type catalyst. It can be said that the arrangements of the copolymer units in the molecular chain are different

from each other.

EXAMPLES

The following examples specifically illustrate the
5 present invention.

[Example 1]

<Preparation of a zirconium catalyst>

Toluene (30 ml) and 2 millimoles of
bis(cyclopentadienyl)zirconium monochloride monohydride were
10 charged into a 100 ml glass flask thoroughly purged with
nitrogen, and formed into a slurry. To the slurry was added
dropwise at room temperature 20 millimoles of trimethyl
aluminum diluted with toluene (1M solution). After the
addition, the mixture was heated to 60°C and maintained at this
15 temperature for 1 hour. The bis(cyclopentadienyl)zirconium
monochloride monohydride dissolved in toluene, and the
solution became dark red. The above reaction was carried out
while shutting off light.

<Preparation of methylaluminoxane>

20 A 400 ml glass flask thoroughly purged with argon was
charged with 13.9 g of magnesium chloride hexahydrate and 125
ml of toluene. After cooling the materials to 0°C, 250
millimoles of trimethyl aluminum diluted with 125 ml of toluene
was added dropwise. After the addition, the temperature was

raised to 70°C, and the mixture was maintained at this temperature for 96 hours. After the reaction, the reaction mixture was subjected to solid-liquid separation by filtration. Toluene was removed under reduced pressure from the separated liquid phase to give 7.3 g of aluminoxane as a white solid. The product has a molecular weight, determined from a freezing point depression in benzene, of 1910 and an m value of 31. At the time of polymerization shown below, the aluminoxane was used after again dissolving it in toluene.

10 <Polymerization>

A 20-liter continuous polymerization reactor was charged continuously with 2 liter/hr of purified toluene, 10 mg-atom/hr, as aluminum atom, of methylaluminoxane and 4×10^{-3} mg-atoms/hr, as zirconium atom, of the zirconium catalyst prepared above. Ethylene, 4-methyl-1-pentane and hydrogen were simultaneously fed continuously into the reactor at the rate of 200 liters/hr, 200 g/hr and 20 liters /hr, respectively, and polymerized at 40°C and atmospheric pressure with a residence time of 0.5 hour under such conditions as to provide a polymer concentration of 35 g/liter. The resulting polymer solution was continuously withdrawn from the reactor, to which small amount of methanol was added to stop the polymerization, and then was transferred into large amount of methanol for precipitation of the polymer. The resulting polymer was dried

at 80°C under reduced pressure for 12 hours. The polymer had an ethylene content of 93.5 mole%, $[\eta]$ of 0.39 dl/g, an (M_w/M_n) of 2.17, a B value of 1.07, a crystallinity of 41.7%, a density of 0.905, the highest melting point of 98.0°C, a softening point
5 of 105.5°C. Signals based on $\alpha\beta$ and $\beta\gamma$ were not observed in the ^{13}C -NMR spectrum of the resulting polymer. The activity of the catalyst was 17500 g of polymer/mg-atom of Zr.

[Examples 2-6]

10 Example 1 was repeated except that the conditions indicated in Table 1 were employed. Signals based on $\alpha\beta$ and $\beta\gamma$ were not observed in the ^{13}C -NMR spectra of the resulting polymers. The results are shown in Table 2.

15 [Comparative Example 1]

<Preparation of a titanium catalyst>

A 400 ml glass flask was charged with 5 g of anhydrous magnesium chloride and 190 ml of purified decane, to which 18.4 ml of ethanol was added dropwise with stirring for 1 hour, the
20 mixture was subsequently maintained at room temperature for 1 hour.

Then 17.2 ml of diethylaluminum chloride was added dropwise thereto for 1 hour. In this time, the reaction system was maintained at 35 to 40°C. After the addition, the mixture was

maintained for 1 hour at room temperature, then 69.2 ml of titanium tetrachloride was added, and maintained at 80°C for 2 hours. After that, the reaction mixture was subjected to solid-liquid separation by hot filtration. The resulting solid
5 was washed with decane repeatedly until Ti is not detected in the wash liquid. The solid catalyst obtained in this way contained 56 mg of Ti/g of the catalyst.

<Polymerization>

A 2-liter autoclave was charged with 720 ml of purified
10 cyclohexane and 280 ml of 4-methyl-1-pentane, and then was charged with hydrogen at the partial hydrogen pressure of 25 kg/cm²(gauge). The mixture was heated to 150°C and 0.4 mg-atm, as aluminum atom, of diethylaluminum chloride, 6×10^{-3} mg-atom, as titanium atom, of titanium catalyst and ethylene were
15 simultaneously fed thereto. Ethylene was supplied to maintain the total pressure in the autoclave at 45 kg/cm²(gauge), polymerization was carried out for 2 hours at 170°C. After the 2 hours, polymerization was stopped by the addition of ethanol to the reaction mixture. The reaction
20 mixture was worked up in the same way as in Example 1. The resulting polymer is 138 g, and the polymerization activity of the catalyst was 23000 g of polymer/mg-atom of Ti. The analytical result of the polymer is shown in Table 2.

EFFECT OF THE INVENTION

The ethylenic random copolymer wax of the present invention has a narrow molecular weight distribution, a narrow composition distribution, and only a small amount of low
5 molecular weight component which makes the molecular weight distribution curve wide-based in shape.

The ethylenic random copolymer wax of the present invention has low stickiness and cohesiveness, therefore suitable for a pigment dispersing agent.

10

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows an example of differential thermal absorption spectrum of an ethylenic random copolymer wax of the present invention.

15

[FIGURE 1]

thermal absorption

20 temperature

TABLE 1

| Monomer 1 | | Monomer 2 | | Hydrogen | | Solvent | | Residence | | Polymerization | | Zr | | Al | | Polymer | | Activity | |
|-----------|----------|-----------|----------|----------|--------|---------|--------|-----------|-------------|----------------|------|------|---------|------|-------|---------------|---------------|----------------|--|
| Type | Amount | Type | Amount | (g/hr) | (l/hr) | (l/hr) | (l/hr) | time | Temperature | (mg-atm | (°C) | (hr) | (mg-atm | (hr) | (g/l) | Concentration | (g of polymer | | |
| | (l/hr) | | | | | | | | | | | | | | | | | /mg-atm of Zr) | |
| Example 1 | Ethylene | 200 | 4MP-1* | 200 | 20 | 20 | 2 | 0.5 | 40 | 0.004 | 10 | 35 | 17500 | | | | | | |
| 2 | " | " | " | " | " | " | " | " | 50 | " | " | 32 | 16000 | | | | | | |
| 3 | " | " | " | 300 | " | " | " | " | " | " | " | 38 | 19000 | | | | | | |
| 4 | " | " | " | 200 | 40 | " | " | " | " | " | " | 10 | 5000 | | | | | | |
| 5 | " | " | 1-hexane | " | 20 | " | " | " | " | " | " | 31 | 15500 | | | | | | |
| 6 | " | " | " | 120 | 40 | " | " | " | " | " | " | 14 | 7000 | | | | | | |

4MP-1*; 4-methyl-1-pentene

TABLE 2

| α -Olefin | Ethylene | $[\eta]$ | Mw/Mn | B Value | Crystallinity | Density | Highest | Softening | |
|----------------------------|----------|----------|-------|---------|---------------|----------------------|------------|-----------|-------|
| | Content | | | | | | Melting | Point | |
| | (mole %) | (dl/g) | | | (%) | (g/cm ³) | Point (°C) | (°C) | |
| Example 1 | 4MP-1* | 93.5 | 0.39 | 2.17 | 1.07 | 41.70 | 0.905 | 98.0 | 105.5 |
| 2 | " | 95.5 | 0.31 | 2.15 | 1.05 | 59.10 | 0.920 | 106.1 | 112.5 |
| 3 | " | 91.7 | 0.27 | 2.13 | 1.09 | 35.40 | 0.892 | 93.0 | 97.5 |
| 4 | " | 94.8 | 0.23 | 2.07 | 1.05 | 53.30 | 0.915 | 105.5 | 110.0 |
| 5 | 1-hexane | 91.6 | 0.32 | 1.95 | 1.09 | 30.20 | 0.888 | 78.3 | 86.5 |
| 6 | " | 94.8 | 0.36 | 2.00 | 1.05 | 47.00 | 0.913 | 101.0 | 107.0 |
| Comparative | | | | | | | | | |
| Example 1 | 4MP-1* | 93.8 | 0.26 | 4.03 | 1.04 | 51.60 | 0.906 | 123.2 | 126.0 |
| 4MP-1*; 4-methyl-1-pentene | | | | | | | | | |